

Contents

1	Introduction	1
2	Radiation–Matter Interaction in the Two-Level System	7
2.1	Introduction	7
2.2	Generality on Radiation–Matter Interaction	7
2.3	Synopsis on the Two-Level Model	12
2.4	Absorption	16
2.5	Nonlinear Absorption	17
2.6	Adiabatic Approximation	21
2.7	Franck–Condon Principle	23
2.8	Beyond Condon Approximation	29
	Appendix 2.A: Two Level Density Matrix	32
	Appendix 2.B: Perturbation Theory Quick Guide	34
	References	34
3	Molecular Exciton	35
3.1	The Molecular Exciton in Aggregates	35
3.1.1	Parallel Dipoles (H-Aggregate)	37
3.1.2	In-Line Dipoles (J-Aggregate)	38
3.1.3	Oblique Dipoles	39
3.1.4	Coplanar Dipoles	39
3.1.5	3D Dipole Geometry ($\theta = 90^\circ$)	40
3.2	Vector Model for the Large Aggregate	45
3.3	Interaction Regimes and Vibrational Dynamics	47
3.4	Quick View on Aggregate Multiexciton States	49
3.5	The Role of Disorder	50
4	Excited States in Solids	53
4.1	On the Origin of Bands in Solids	53
4.2	Excitons	58
4.2.1	Frenkel Exciton	59

4.2.2	The Wannier–Mott Exciton	63
4.2.3	1D Excitons	67
5	Photoexcitation Dynamics	71
5.1	Photoexcitation and Relaxation Scenario in Inorganic Semiconductors	71
5.1.1	Link to Photovoltaic	73
5.2	Confined States in Semiconducting Nanocrystals	73
5.3	Carrier Multiplication in Nanocrystals	78
5.4	The Excitation Zoo in Molecular Semiconductors	79
5.4.1	Free Carriers	79
5.4.2	Trapped Carriers	80
5.4.3	Polarons	80
5.4.4	Bipolaron	81
5.4.5	Polaron Pair	81
5.4.6	Charge Transfer State	82
5.4.7	CT Exciton	82
5.4.8	Wannier–Mott Exciton	82
5.4.9	Trion (Charged Exciton)	83
5.4.10	Frenkel Excitons	83
5.4.11	Excited Molecular State	83
5.5	Conjugated Polymers	83
	References	87
6	Photophysics Tool Box	89
6.1	Jablonski Diagram	89
6.2	Strickler–Berg Relationship	91
6.3	Energy Migration and Transfer	96
6.3.1	Radiative Migration	98
6.3.2	Nonradiative Energy Transfer	99
6.4	The Vavilov–Kasha Rule	103
6.5	The Gap Law and Radiationless Transitions in Molecules	105
6.6	Rate Equations	112
6.7	Triplet Generation	114
6.7.1	Spin Flip	115
6.7.2	Radical Pair Recombination	118
6.7.3	Singlet Fission	120
	Appendix 6.A: Derivation of the Strickler–Berg Relation	122
	References	123
7	Vibrational Spectroscopy	125
7.1	The Semiclassical Picture of the Interaction of Light with Molecules	125
7.2	Derivation of the Correlation Function	129
7.3	The Full Vibronic Correlator in Time	130

7.4	Raman Scattering	131
7.5	Coherent Phonons	136
	References	143
8	Charge Transfer and Transport	145
8.1	Adiabatic Electron Transfer: Classical Marcus Theory	145
8.2	Quantum Mechanical Expressions for Electron Transfer: Nonadiabatic Multiphonon Regime	149
8.3	The Donor–Acceptor Interface	151
8.4	Charge Photogeneration in Excitonic Semiconductors	152
8.5	Synopsis on Transport	159
8.5.1	Experiments to Measure Mobility	163
8.5.1.1	Time of Flight (ToF)	163
8.5.1.2	Photoconductivity	164
8.5.1.3	Field Effect Transistor (FET)	166
8.5.1.4	Pump Probe	167
8.5.1.5	Diode	170
8.5.1.6	Optical Transitions	171
8.5.2	Extended versus Localized States	173
	References	176
9	Pump Probe and Other Modulation Techniques	177
9.1	Electroabsorption	177
9.2	Pump Probe	181
9.3	cw Photoinduced Absorption	193
	Appendix 9.A: Pump Probe in the Two-Level System	198
	Appendix 9.B: The Coherent Coupling in Degenerate Pump Probe	200
10	Conclusion	205
	Bibliography	209
	Index	211